

## DISTRIBUTION OF $p\text{CO}_2$ AND $\delta^{13}\text{C}$ IN THE AIR AND SURFACE SEA WATER IN THE SOUTHERN OCEAN, SOUTH OF AUSTRALIA

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**Abstract:** Distribution of  $p\text{CO}_2$  and  $\delta^{13}\text{C}$  in the air over the ocean and in the surface sea water of the Southern Ocean was determined during the cruise of BIOMASS (November 1983 to February 1984). In the study area, south of Australia,  $p\text{CO}_2$  in the air was nearly constant ( $\sim 342$  ppm) throughout the cruise but  $p\text{CO}_2$  in the surface sea water varied considerably ranging from 300 to 356 ppm. In general,  $p\text{CO}_2$  in the surface sea water tended to increase from north to south, and it was relatively higher than that in the air in higher latitudes. The average value in the south of  $5^\circ\text{S}$  was  $-7.97\text{‰}$  for  $\delta^{13}\text{C}$  and 341.7 ppm for  $p\text{CO}_2$  of atmospheric  $\text{CO}_2$ . These results indicate that atmospheric  $\text{CO}_2$  over the ocean is not isotopic equilibrium with the surface sea water and kinetic fractionation must be considered for understanding  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$ .

### 1. Introduction

Recent increase of the atmospheric  $\text{CO}_2$  concentration has attracted the great public concerns as one of the triggers for the global climatic change in the near future. The increasing rate of the atmospheric  $\text{CO}_2$ , however, does not reflect directly the estimated amount of the  $\text{CO}_2$  release through the combustion of fossil fuel. The amount of the increase in the air is estimated to be 55% of all fossil  $\text{CO}_2$  produced during the period from 1959 to 1978 (ROTTY, 1983).

The exchange of  $\text{CO}_2$  among the main terrestrial carbon reservoirs (atmosphere, biosphere and hydrosphere) controls the material balance of  $\text{CO}_2$  in the earth's environment, but little is known about the magnitude of the contribution of  $\text{CO}_2$  exchanges between air/sea or air/biota to the change of atmospheric  $\text{CO}_2$ .

The measurement of the partial pressure of  $\text{CO}_2$ ,  $p\text{CO}_2$ , in the surface sea water is one of the essential requirements for understanding the global carbon cycle. Based on the IGY data, KEELING (1968) has constructed a rough sketch of  $p\text{CO}_2$  distribution in the world oceans, and later MIYAKE *et al.* (1974) have given a horizontal distribution of  $p\text{CO}_2$  in the Pacific Ocean in detail.

The results of these works indicate that  $p\text{CO}_2$  in the surface sea water was supersaturated with respect to  $p\text{CO}_2$  in the air in the equatorial region and undersaturated in the subtropical region except in the area where upwelling occurs. It is often treated that water in high latitudes is a sink of the excess  $\text{CO}_2$  by the direct ventilation of intermediate and deep waters to the surface air (SIEGENTHALER, 1983), whereas the Antarctic Ocean has been reported to be supersaturated with respect to the atmosphere as given by TORII *et al.* (1959) and MIYAKE and SUGIMURA (1969).

The seasonal, secular and regional trends of pCO<sub>2</sub> in the Southern Ocean, however, still remain ambiguous. During the Southern Cross Cruise (KH-68-4, November 1968 to February 1969), pCO<sub>2</sub> in the surface sea water and air over the ocean in the south of New Zealand was measured by one of the authors, SUGIMURA (MIYAKE *et al.*, 1974), but there has been no information on the pCO<sub>2</sub> and  $\delta^{13}\text{C}$  values in the air and sea water in the south of Australia up to the present.

In the present paper, the authors intend to report the results of measurements of pCO<sub>2</sub> in the air and surface sea water together with  $\delta^{13}\text{C}$  in the air mainly from 5° to 65°S along 150°E. The results clearly indicate that the Southern Ocean water is not equilibrated with the atmosphere with respect to both pCO<sub>2</sub> and  $\delta^{13}\text{C}$ .

## 2. Samples and Method of Analysis

The measurements of pCO<sub>2</sub> in the air and surface sea water, and the sampling of air for the measurement of  $\delta^{13}\text{C}$  were carried out on board the R. V. HAKUHO MARU which belongs to the Ocean Research Institute, University of Tokyo, during the cruise of BIOMASS 1983–1984 (KH-83-4) along the course from the western North Pacific to the Southern Ocean and back home through the Indian Ocean. The track of the cruise is illustrated in Fig. 1.

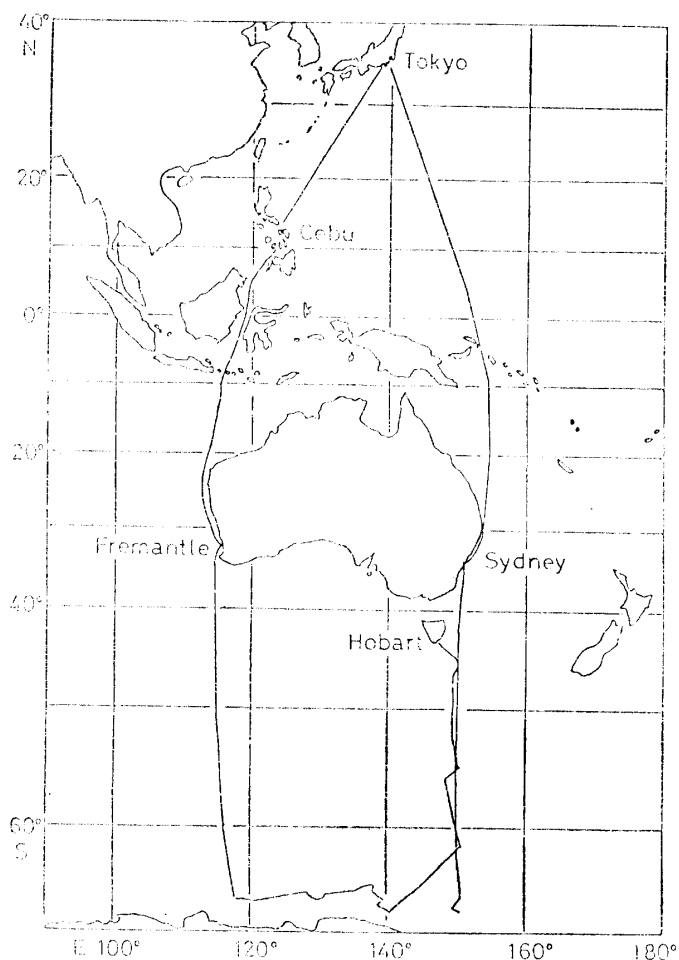


Fig. 1. Track of BIOMASS 1983 cruise (November 1983 to February 1984).

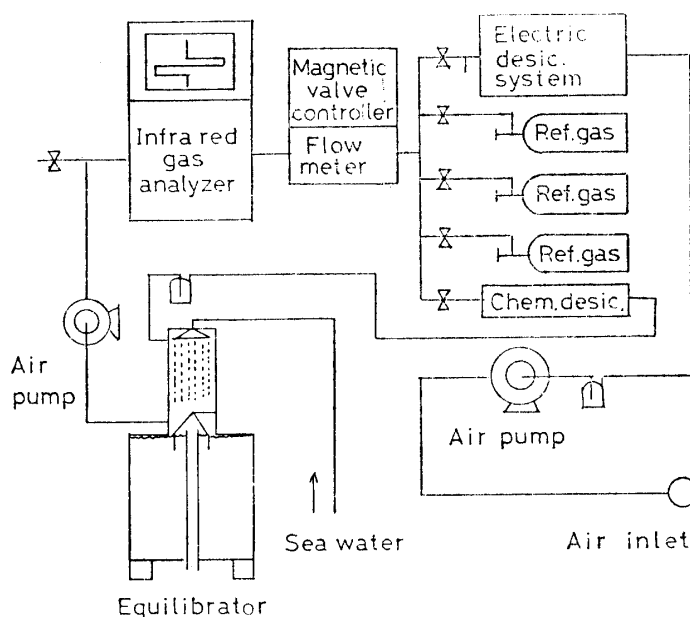


Fig. 2. A schematic diagram of the  $\text{CO}_2$  measurement system in the air and the surface sea water.

The continuous records of  $\text{pCO}_2$  in the air and sea water were taken in the round trip from Tokyo (November 1983) to Tokyo (February 1984). The schematic drawing of the instrument used for the measurements of  $\text{pCO}_2$  in the air and surface sea water is given in Fig. 2. Sea water was pumped up continuously from 5 m below the sea surface (bottom of the ship) and introduced into an equilibrator in a closed circuit consisting of a diaphragm air pump, an electric dehumidifier, with chemical desiccant and gas exchange column. Correction was made for the observed  $\text{pCO}_2$  value of the surface sea water following eq. 1 (GORDON and JONES, 1973) which is caused by the warming of sea water sample through the inner piping.

$$\frac{\delta \text{pCO}_2}{\delta T} = 4.4 \times 10^{-2} \text{pCO}_2 - 4.6 \times 10^{-6} (\text{pCO}_2)^2, \quad (1)$$

where  $T$  is the temperature of the sea water and the value of  $\text{pCO}_2$  is expressed as mole fractions in parts of  $\text{CO}_2$  per million parts of dry air (ppm).

The air sample was collected about 5 m above the sea level at the bow of the vessel with a rate of  $5 \text{ l min}^{-1}$ . About one-tenth of the sample air was introduced into the sample cell of a non-dispersive infrared gas analyzer (Beckman model 315A). For the calibration of the instrument, three different concentrations of working standard gases ( $\text{CO}_2/\text{N}_2$ ) were used: two (250 and 450 ppm) were passed through five minutes each every hour and the rest (350 ppm) every two or three days to confirm the calibration curve used for the conversion from mV to ppm. The working standard gases were calibrated against the primary standard gases ( $\text{CO}_2/\text{Air}$ ) prepared by the gravimetric method. The primary standard gases were standardized against the WMO standard (1981 mole fraction, supplied from the Scripps Institution of Oceanography). The accuracy of the measurement was estimated to be  $\pm 0.6$  ppm by a duplicate analysis of the same air sample.

For the measurement of carbon isotopic ratio, sample air was collected intermittently in a plastic bag with continuous monitoring of pCO<sub>2</sub> from Tokyo to Cebu, Philippines. Within several hours after sampling, CO<sub>2</sub> in the air was concentrated in a trap with fritted glass disk immersed in liquid nitrogen under the reduced pressure. The CO<sub>2</sub> deposited in the trap was purified by the cryogenic distillation and transferred into a sample tube.

The isotopic composition of carbon was measured on a tripple ion collector mass spectrometer (Finnigan Mat 250) at the Meteorological Research Institute. The results of the measurement were expressed as the per mil deviation from the PDB standard:

$$\delta^{13}\text{C} = \left[ \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{PDB}}} - 1 \right] \times 10^3. \quad (2)$$

The instrument was calibrated against the international reference standard NBS-20 ( $\delta^{13}\text{C} = -1.06\text{‰}$ ). A duplicate analysis of the same standard and the sample air revealed that the standard deviation of the analytical results was  $\pm 0.05\text{‰}$  for the observed  $\delta^{13}\text{C}$  value.

Correction due to N<sub>2</sub>O which is trapped at the same time with CO<sub>2</sub> and interferes the isotopic measurement is not given in this report because of the unknown concentrations of N<sub>2</sub>O in maritime air. On our mass spectrometer, the beam intensity of mass 44 ion of N<sub>2</sub>O<sup>+</sup> was about 71% to that of CO<sub>2</sub><sup>+</sup> at equal inlet pressure (INOUE and SUGIMURA, 1984). The ionization efficiency of N<sub>2</sub>O is lower than that of CO<sub>2</sub> (MOOK and VAN DER HOEK, 1983). If N<sub>2</sub>O concentration is 0.3 ppm, the correction of 0.23‰ is given for the observed  $\delta^{13}\text{C}$  value (CRAIG and KEELING, 1963).

### 3. Results and Discussion

The results of the determination of pCO<sub>2</sub> value in the surface sea water along 150°E are shown in Fig. 3. During the back and forth cruises along the line from 45 to 65°S, pCO<sub>2</sub> in the surface sea water was measured repeatedly in the same area three times within 30 days. As seen in the figure, pCO<sub>2</sub> in the surface sea water increased from north to south, and it is relatively higher than that in the air ( $\sim 342$  ppm) in high latitudes. The partial pressure of CO<sub>2</sub> in the surface sea water changed at the subtropical convergence (47°S), the subantarctic front (49°S) and polar front (56.5°S). As is well-known, the water temperature decreased from north to south along the observation line but pCO<sub>2</sub> in the surface sea water increased significantly from the subtropical to the polar front.

Following the geographical location of oceanographic fronts, the area was divided into four sections and the average value of pCO<sub>2</sub> in the surface sea water in each area is given in Table 1. In the circumpolar water, the pCO<sub>2</sub> value in the surface water varied significantly from place to place. An example of the distribution of pCO<sub>2</sub> is shown in Fig. 4 along 65°S from 115 to 150°E. As seen in the figure, the pCO<sub>2</sub> value ranged from 330 to 380 ppm and it is noted that most of the surface sea water was supersaturated with respect to the atmospheric CO<sub>2</sub> (341.7 ppm).

Therefore, it can be said that the Antarctic Ocean acts as a source of CO<sub>2</sub> at least during the early summer in the south of Australia region. A fairly uniform distribu-

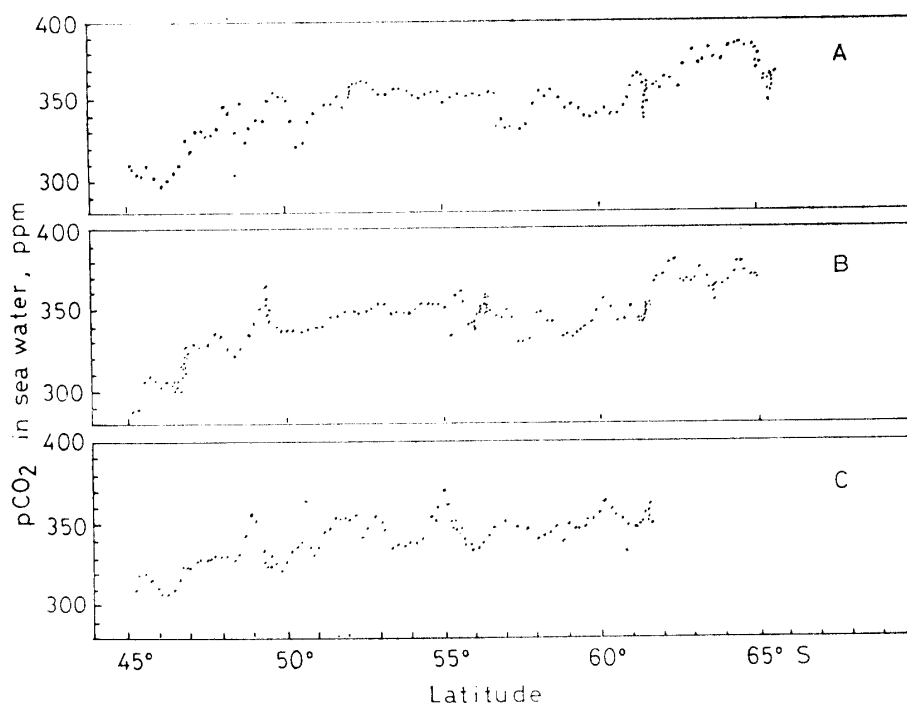


Fig. 3. Distribution of  $p\text{CO}_2$  in the surface sea water along  $150^\circ\text{E}$  in the Southern Ocean. A: southward traverse, B: northward traverse, C: southward traverse.

Table 1. The average values of  $p\text{CO}_2$  in the surface sea water in the Southern Ocean divided into four areas based on geographic locations of oceanographic fronts along  $150^\circ\text{E}$  (unit ppm).

	45–47°S	47–49°S	49–56.5°S	56.5°S–
A	$300.8 \pm 10.3$	$332.6 \pm 8.7$	$350.0 \pm 9.0$	$356.4 \pm 14.3$
B	$309.7 \pm 10.0$	$328.6 \pm 4.3$	$348.5 \pm 7.2$	
C	$314.5 \pm 7.1$	$334.0 \pm 8.3$	$342.9 \pm 10.4$	$355.8 \pm 8.7$

A: Southward traverse, B: northward traverse, C: southward traverse.

tion of inorganic nutrients with depth strongly indicates that the enhanced vertical mixing and biological activity in this region may be responsible for maintaining relatively high  $p\text{CO}_2$  values.

Zonal mean values of  $p\text{CO}_2$  and  $\delta^{13}\text{C}$  in the air from  $5^\circ\text{S}$  to the Antarctic Ocean are given in Table 2. The area was divided into four parts tentatively. As seen in the table,  $p\text{CO}_2$  in the air in the southern hemisphere showed a fairly uniform distribution in the meridional direction with the average value of 341 to 342 ppm. The  $\delta^{13}\text{C}$  value of the atmospheric  $\text{CO}_2$  in the southern hemisphere tended to increase from  $-8.03$  to  $-7.88\text{‰}$  with latitude.

Thus, the relationship between  $p\text{CO}_2$  and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in the air over the ocean is different from that in the continental and forest air, where  $\delta^{13}\text{C}$  of the atmospheric  $\text{CO}_2$  is linearly correlated with the reciprocal of  $p\text{CO}_2$  (FREYER, 1979; KEELING, 1958, 1961; INOUE and SUGIMURA, 1984).

Variations in  $\text{CO}_2$  in the forest air are caused by air/biota  $\text{CO}_2$  exchange and that

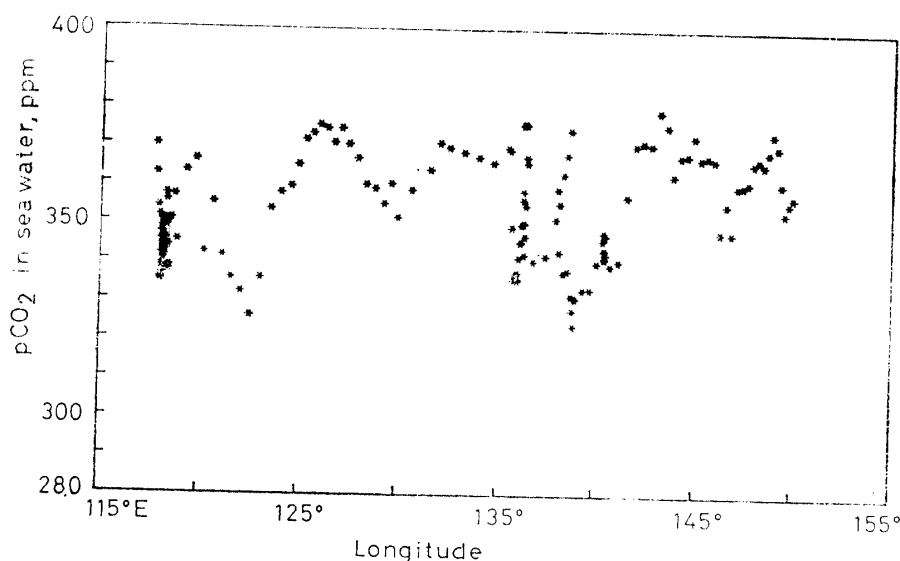


Fig. 4. Distribution of pCO<sub>2</sub> in the surface sea water around 65°S, south of Australia.

Table 2. The average value of pCO<sub>2</sub> and  $\delta^{13}\text{C}$  in the air over the South Pacific and the Southern Ocean.

Area	pCO <sub>2</sub> (ppm)	$\delta^{13}\text{C}$ (‰)	Sample number
5–40°S	341.8±0.5	−8.03±0.09	6
40–50°S	341.5±0.5	−8.08±0.13	4
50–60°S	341.7±0.4	−7.98±0.16	6
60°S–	341.6±0.9	−7.88±0.24	10

in the continental air by fossil fuel CO<sub>2</sub>. The reason of the difference of the relationship in the marine air from the “single mixing relation” in the forest and continental air is a problem for the further study, but it may be related to some other process of carbon cycle; such as air/sea exchange.

In general, carbon isotopic composition in the air CO<sub>2</sub> changes when the exchange of CO<sub>2</sub> takes place between the air and the sea water. The equilibrium fractionation factor of carbon isotopes between the air and the sea water increases with decreasing temperature (INOUE and SUGIMURA, 1985a; KROOPNICK, 1974).

Considering the meridional distribution of the  $\delta^{13}\text{C}$  value in the air CO<sub>2</sub> over the ocean, there are about 30 K difference of temperature in the north-south direction. Thus the  $\delta^{13}\text{C}$  value in the air CO<sub>2</sub> is expected to vary from −8.6‰ at 273.2 K to −5.1‰ at 303.2 K in equilibrium under the condition that  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  in the sea water is 2‰.

However, as seen in Table 2, the  $\delta^{13}\text{C}$  value in the air CO<sub>2</sub> is fairly constant with latitude, and it is deviated negatively in the tropical to subantarctic area and positively in the antarctic from the expected value under the isotopic equilibrium between the air and the sea water at given temperature.

The results of previous studies (KEELING *et al.*, 1979; MOOK *et al.*, 1983) indicate that  $\delta^{13}\text{C}$  of the air CO<sub>2</sub> in a remote area has been decreasing with the increase of CO<sub>2</sub>, and further,  $\delta^{13}\text{C}$  of the atmospheric CO<sub>2</sub> in almost all ocean area tends to increase the deviation from the isotopic equilibrium value with that of  $\Sigma\text{CO}_2$  (KROOPNICK, 1985) in the surface sea water.

Therefore, equilibrium process cannot explain the observed results of  $\delta^{13}\text{C}$  and  $\text{CO}_2$  in the air over the ocean.

For further treatment of carbon cycle, we must consider the kinetic isotope exchange process between the air and the sea water. The result of recent study (INOUE and SUGIMURA, 1985a) indicates that the kinetic isotope fractionation factor of  $^{13}\text{C}$  from the air to the sea water is larger than that of the sea to the air, and the estimated value of carbon isotopic ratio of  $\text{CO}_2$  passing through the air/sea interface is given to be  $-10\text{‰}$  for air-to-sea and  $-8\text{‰}$  for sea-to-air, when the  $\text{CO}_2$  exchange takes place between the air ( $\delta^{13}\text{C} = -8\text{‰}$ ) and the surface sea water ( $\delta^{13}\text{C} = 2\text{‰}$ ) at 288.2 K.

It appeared that for the purpose of qualitative explanation of the observed  $\delta^{13}\text{C}$  value in the air over the ocean, the process of kinetic exchanging is much more reasonable than equilibrium process as regarded for a long time by many researchers.

#### 4. Conclusion

The Antarctic Ocean cannot be treated simply as a sink of excess  $\text{CO}_2$  released by the increased human activities in recent years (SIEGENTHALER, 1983) because  $\text{pCO}_2$  in the surface sea water was higher than that in the air at least during the early summer in the south of Australia region.

The results of carbon isotopic measurement of atmospheric  $\text{CO}_2$  indicate that  $\text{CO}_2$  exchange between the air and the sea water must be considered under the concept of kinetic exchange process based on the difference in  $\text{pCO}_2$  between the air and the sea water.

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